

for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 11.2.1 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated  $\text{HNO}_3$ . Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning Section 8.3.3.

8.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated  $\text{HNO}_3$  to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated  $\text{HNO}_3$ , 4 ml of concentrated HF, and then continuing to follow the procedures described in Section 8.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 8.3.1.2. The resultant combined sample is referred to as "*Sample Fraction 1*". Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is "*Analytical Fraction 1*". Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as "*Analytical Fraction 1B*". Label the remaining 250-ml portion as "*Analytical Fraction 1A*". Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

8.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample to within 0.5 ml and label it "*Sample Fraction 2*". Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot "*Analytical Fraction 2B*". Label the remaining portion of Container No. 4 as "*Sample Fraction 2A*". Sample Fraction 2A defines the volume of Analytical Fraction 2A prior to digestion. All of Sample Fraction 2A is digested to produce "*Analytical Fraction 2A*". Analytical Fraction 2A defines the volume of Sample Fraction 2A after its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated  $\text{HNO}_3$  by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the

digestion procedures described in Sections 8.3.4.1 or 8.3.4.2.

8.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent  $\text{HNO}_3$ , and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent  $\text{H}_2\text{O}_2$  and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

8.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent  $\text{HNO}_3$ , and heat for 6 minutes total heating time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in Section 8.3.1. Allow the sample to cool. Add 10 ml of 3 percent  $\text{H}_2\text{O}_2$  and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

NOTE: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

8.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be Analytical Fraction 3A. To remove any brown  $\text{MnO}_2$  precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown  $\text{MnO}_2$  precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown  $\text{MnO}_2$  precipitate, into an appropriately sized vented container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the  $\text{MnO}_2$ , add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown  $\text{MnO}_2$

from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

#### 9.0 Quality Control

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in Sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per Section 8.3.1, 100 ml from Container No. 7 per Section 8.3.2, and 100 ml from Container No. 8A per Section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per Section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in Section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown  $\text{MnO}_2$  precipitate from the blank for Analytical Fraction 3B by the same procedure as described in Section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per Section 11.1.1 and/or Section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per Section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate anal-

yses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP-MS Analysis. Follow the respective quality control descriptions in Section 8 of Methods 6010 and 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent, analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F.

#### 10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

10.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in Section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

#### 11.0 Analytical Procedure

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29-3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP-MS or AAS analysis as described in Sections 11.1.1 and 11.1.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in Section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the H<sub>2</sub>SO<sub>4</sub>/KMnO<sub>4</sub> Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in Section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical

Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in Section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29-2. These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29-3 to determine which techniques and procedures to apply for each target metal. Use Table 29-3, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to Section 10.3 and follow the quality control procedures specified in Section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Analysis*, 15th Edition, Method 303F, or, optionally using NOTE No. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see NOTE No. 1 at end of this section). The total amount of Hg in the aliquot shall be less than 1 µg and within the range (zero to 1000

ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See NOTE No. 2 at the end of this section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent  $\text{HNO}_3$  (1.5 ml concentrated  $\text{HNO}_3$  per liter aqueous solution) so that when a 1- to 10-ml aliquot of the "0.15  $\text{HNO}_3$  percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE NO. 1: When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29-1, select a 10 ml aliquot for digestion and analysis as described.

NOTE NO. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this section: (*The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.*); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

## 12.0 Data Analysis and Calculations

### 12.1 Nomenclature.

A = Analytical detection limit,  $\mu\text{g}/\text{ml}$ .  
 B = Liquid volume of digested sample prior to aliquotting for analysis, ml.  
 C = Stack sample gas volume,  $\text{dscm}^3$ .  
 $C_{a1}$  = Concentration of metal in Analytical Fraction 1A as read from the standard curve,  $\mu\text{g}/\text{ml}$ .  
 $C_{a2}$  = Concentration of metal in Analytical Fraction 2A as read from the standard curve, ( $\mu\text{g}/\text{ml}$ ).  
 $C_s$  = Concentration of a metal in the stack gas,  $\text{mg}/\text{dscm}$ .  
 D = In-stack detection limit,  $\mu\text{g}/\text{m}^3$ .

$F_a$  = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see Section 8.3.4.)

$F_d$  = Dilution factor ( $F_d$  = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading  $C_{a1}$ . For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range,  $F_d = 5$ ).

$\text{Hg}_{\text{bh}}$  = Total mass of Hg collected in the back-half of the sampling train,  $\mu\text{g}$ .

$\text{Hg}_{\text{bh}2}$  = Total mass of Hg collected in Sample Fraction 2,  $\mu\text{g}$ .

$\text{Hg}_{\text{bh}3(\text{A,B,C})}$  = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C,  $\mu\text{g}$ .

$\text{Hg}_{\text{bbb}}$  = Blank correction value for mass of Hg detected in back-half field reagent blanks,  $\mu\text{g}$ .

$\text{Hg}_{\text{fh}}$  = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1),  $\mu\text{g}$ .

$\text{Hg}_{\text{fbb}}$  = Blank correction value for mass of Hg detected in front-half field reagent blank,  $\mu\text{g}$ .

$\text{Hg}_t$  = Total mass of Hg collected in the sampling train,  $\mu\text{g}$ .

$M_{\text{bh}}$  = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2),  $\mu\text{g}$ .

$M_{\text{bbb}}$  = Blank correction value for mass of metal detected in back-half field reagent blank,  $\mu\text{g}$ .

$M_{\text{fh}}$  = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1),  $\mu\text{g}$ .

$M_{\text{fbb}}$  = Blank correction value for mass of metal detected in front-half field reagent blank,  $\mu\text{g}$ .

$M_i$  = Total mass of each metal (separately stated for each metal) collected in the sampling train,  $\mu\text{g}$ .

$M_t$  = Total mass of that metal collected in the sampling train,  $\mu\text{g}$ ; (substitute  $\text{Hg}_t$  for  $M_t$  for the  $\text{H}_2$  calculation).

$Q_{\text{bh}2}$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis. NOTE: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to Section 11.1.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for  $Q_{\text{bh}2}$ .

$Q_{\text{bh}3(\text{A,B,C})}$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis (see NOTES in Sections 12.7.1 and 12.7.2 describing the quantity "Q" and calculate similarly).

$Q_{\text{fh}}$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis. NOTE: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to Section 11.1.3 and its NOTES Nos. 1 and 2), then calculate